CONTROL AND ORIGIN OF NOx IN THE FCCU REGENERATOR
THE PERFORMANCE OF XNOx-2, A COMMERCIAL NOx REDUCTION CATALYST

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Introduction

In this paper we describe the performance of a NOx control additive for the FCCU
regenerator. This formulation reduces NOx and at the same time functions as a CO
oxidation promoter. The NOx reduction catalyst is added to the total FCC inventory at
levels similar to combustion promoter. This promoter has been pilot unit tested in the
Davison circulating riser, and the results have been confirmed in commercial testing.
Laboratory results suggest that these catalysts decrease NO emissions by chemically
reducing the NO with CO in the regenerator to form N_2 and CO_2. While this reaction
also occurs to a certain extent in commercial regenerator operation, it is not catalyzed
by conventional platinum based CO oxidation promoters.

The Chemistry of NOx in the FCCU Regenerator

The major environmental pollutants from burning coke in the FCCU regenerator
include CO (carbon monoxide) and nitrogen and sulfur oxides. Both CO and SOx
emissions can be controlled to a low level using relatively small amounts of commercial
additives. NO_x emissions are also regulated, but are not so easily controlled. NOx
emissions, including NO, NO_2 and N_2O, are typically in the range of 100 ppm to 500
ppm. Since regulations based on regional considerations vary from state to state and
even from refinery to refinery, emissions in this range may be outside allowable limits.
The NO_2 is formed only after the NO is emitted to the atmosphere, while N_2O is formed
in small quantities if at all. Since most of the nitrogen oxides in the regenerator are in
the form of NO, the formation and control of NO in the regenerator is the major issue.

The chemistry of NO in the regenerator has recently been described in two
independent studies (1,2). Both studies agree in essentials. About half of the nitrogen
in the feed appears as coke on the catalyst. The NO in the regenerator derives entirely
from burning the nitrogen in the coke during regeneration. At the relatively low
temperature in the regenerator, $\leq 800°C$, thermodynamic considerations show that NO
is not formed from oxidation of the nitrogen in the air introduced into the regenerator.

The surprise is that only a small percentage of the coke nitrogen is converted to NO
during regeneration. Under normal unpromoted regenerator operation most of the
nitrogen is converted to N_2. These results were obtained by nitrogen balancing a pilot
plant scale FCCU (3) using a relatively high nitrogen feed stock, 0.32% N at relatively
high conversions. The catalyst was regenerated using an argon oxygen mixture in
place of air, eliminating all sources of molecular nitrogen in the regenerator except from
the coke, Table 1.

**Table 1.** Nitrogen Balance in a pilot plant FCCU. Regeneration with an Ar/O_2 mixture.

Feedstock:	Moderate Nitrogen	High Nitrogen
N, Wt%	0.13	0.32
Wt. % Conversion	73.9	59.8
Coke, Wt. % of Feed	3.68	4.26
Flue Gas NO,	62 ppm	211 ppm
Flue Gas N_2,	450 ppm	1250 ppm
Recovery of Feed N, %		
in Total liquid product	47.4	50.1
in Coke	35	-
% of Feed N recovered as NO	2.6	2.7
as N_2	38	32.7
Recovery of Regenerator N, %	5	7
as N_2	95	93
as NO	5	7
Total N Recovery, Wt. %	88.0	85.6

In this experiment the molecular nitrogen formed in the regenerator was directly measured by gas chromatography. The results show that more than 90% of the nitrogen in the coke forms N_2 rather than NO in an unpromoted regenerator. This means that the nitrogen in the coke is either converted directly to N_2 during regeneration, or is converted to NO and then reduced in the regenerator to N_2. The regenerator contains a variety of reductants including carbon monoxide (CO) and unburned coke on catalyst that has just entered the regenerator as well as residual coke on regenerated or partially regenerated catalyst. CO is present in relatively high concentrations, especially in an unpromoted operation. Although the NO can react with both the coke and the CO, the reaction with the CO to form N_2 and CO_2 is probably the most important. These events explain the observed increase in NO emissions with the addition of CO combustion promoter (less CO in the regenerator), and the decrease in NO_x levels observed with operation in partial burn conditions due to increased amounts of CO as well as coke. A number of NO_x reduction strategies including regenerator design changes based on this chemistry have been described in the patent literature. Some are based on placing more reductant in the regenerator, and in other cases the regenerator flue gas contacts reductant in the form of CO or spent catalyst (4-8).

The Reduction of NO with CO or with Coke on Spent Catalyst.

Previous work has shown that the reaction of NO with coke to form N2 is nearly as rapid as the reaction of oxygen with coke (9). We were able to directly observe the reaction of NO with coke on a spent FCCU catalyst under approximate regenerator conditions, Figure 1.

Figure 1: Reaction Between NO and Coke on Spent Catalyst to form Molecular Nitrogen and CO.
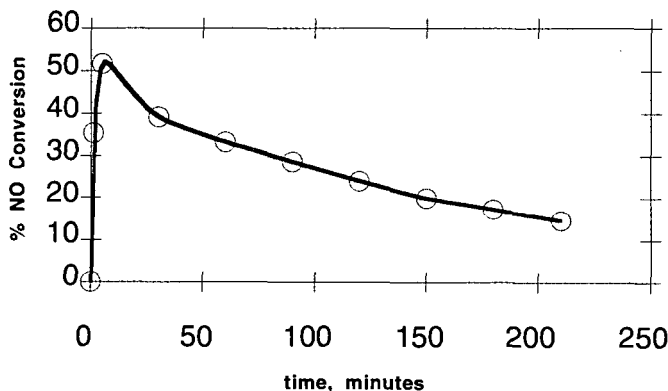
The result of this experiment shows a stiochiometry of approximately 1:1 consistent with the reaction

$$2\,C + 2\,NO = 2\,CO + N_2.$$
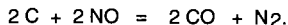
Another possibility is the reduction of NO with CO in the regenerator. Reactor studies show that while NO and CO do not react at regenerator temperatures in an empty reactor or over a low surface area inert, the reaction will occur over equilibrium catalyst, especially with nickel, vanadium and possibly other contaminants. Previous work has shown that high nickel equilibrium catalysts can function as CO oxidation promoters (10). Vanadium on titania is a well known commercial SCR catalyst. This result shows that equilibrium catalysts containing metal can also function as a promoter for the reaction of CO with NO, Table 2.

Table 2. Activity for NO conversion by reduction with CO. Reaction conditions
9,000 GHSV, 1700 ppm NO, CO/NO = 3/1.

Equilibrium Catalyst	A	B
Ni, ppm	378	1598
V, ppm	471	2298
Reactor Temperature, °C	**% Conversion**	
550	0.0	0.0
673	9	24
711	9	45
732	9	56

NO emissions can be reduced by reaction with CO in the regenerator or coke on the catalyst. These reactions form the basis for commercial strategies for NO control such as operation in partial burn, operation with low levels of promotion and higher levels of CO, and a variety of patented processes. However, it is not generally desirable to sacrifice CO conversion or to increase coke on regenerated catalyst for the sake of NOx reduction. Since NOx emissions increase with the addition of CO oxidation promoter, it is important to develop a promoter which catalyzes both the oxidation of CO to CO_2 as well as the reduction of NO to N_2 with CO. The operation of such a promoter, XNOx-2, in a FCC pilot unit is shown in Figure 2. The pilot unit operation is the Davison Circulation Riser (DCR) described elsewhere (11) running a feed stock previously described (1) containing 0.13 wt. % nitrogen.

Figure 2: Comparison of NO emissions in the DCR (Davison Circulating Riser)with a circulating catalyst inventory containing 0.5% of 500 ppm Pt on alumina (x) and 0.5% of XNOx-2 (o).
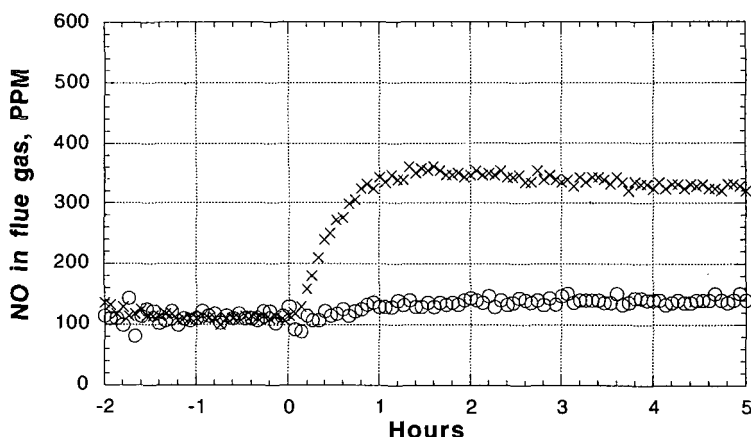


XNOx-2 and Pt/Alumina Activity for NO Reduction by CO

XNOx-2 works by providing a balanced bifunctional catalytic activity for both the oxidation of CO to CO_2 and for the reaction of CO with NO to produce CO_2 and N_2, controlling both CO and NO emissions. To demonstrate the catalytic basis for this effect we passed CO and NO over XNOx-2 and over a conventional CO combustion promoter containing 500 ppm Pt impregnated on alumina with the results shown in Figures 3 and 4. The activity for CO conversion in the presence of NO over platinum flattens and drops off over 400 °C, while the activity for this reaction over XNOx-2 increases rapidly up to at least 600°C, the highest temperature tested, Figure 3a. The NO conversion plot with temperature shows the same trend, Figure 3b. In this experiment the platinum promoter cannot convert more than 50% of the NO, while the XNOx-2 converts essentially all of the NO. By comparison conversion over Ecat is an order of magnitude or more lower, Table 2.

A plot of CO conversion on one axis and NO conversion on the other axis, Figure 4, is especially interesting. In the case of XNOx-2 we obtain a 45° plot showing one to one conversion. This agrees with the proposed stoichiometry. For every molecule of NO converted, one molecule of CO is converted, the stoichiometry for the desired reaction

$$2CO + 2NO \longrightarrow 2CO_2 + N_2.$$

Over the platinum promoter more NO is converted than CO. This indicates the conversion of NO to nitrogen species other than N_2. The platinum based CO promoters do not promote the reaction between NO and CO very effectively at regenerator temperatures, and the product is not the desired N_2. XNOx-2, on the other hand, is selective for the conversion of NO to N_2 in the presence of CO and at regenerator temperatures.

Figure 3: CO and NO conversion over 500 ppm Pt on gamma alumina (x) and over XNOx-2 (o) at 25,000 GHSV, 1375 ppm NO, and 3000 ppm CO.
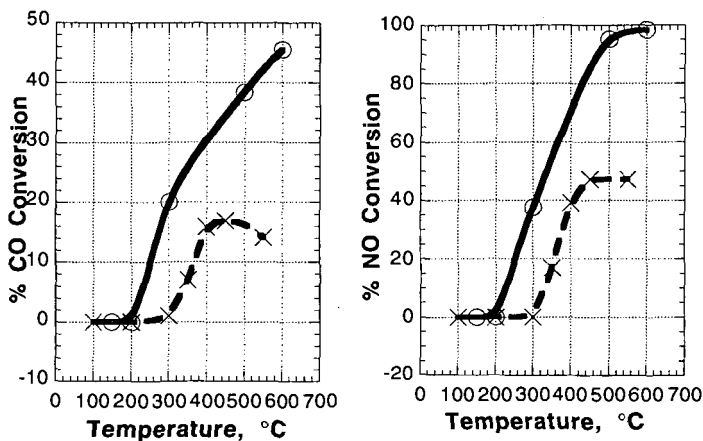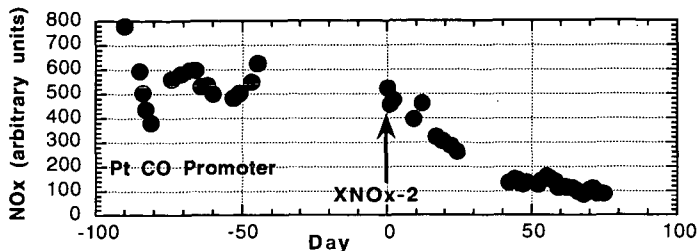

Figure 4: CO and NO stiochiometry for the results in Figure 3.
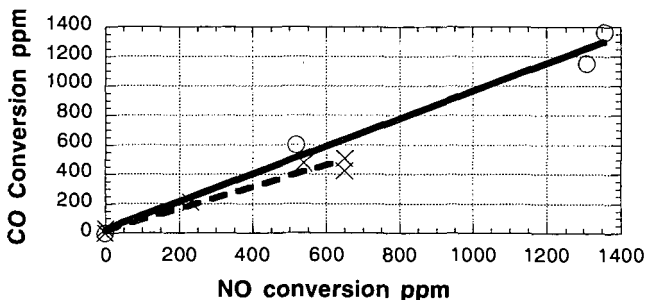
Commercial Testing

XNOx-2 has been tested in a commercial application currently using a conventional Pt on alumina CO combustion promoter. The conventional combustion promoter was discontinued and XNOx-2 begun at day zero shown in Figure 5. NOx emissions decreased slowly over a period of thirty days from a level of 500 units to a level of about 150 units, a drop of about 70%. During this period of time the afterburn, a measure of CO promotion efficiency, remained within normal limits. The commercial NOx reduction is somewhat greater than observed in DCR testing. The reason for this is probably the poorer mixing and higher localized CO concentrations in the commercial regenerator. In regions of high CO concentration the XNOx-2 will be especially effective.

Figure 5: Commercial test of the combustion promoter XNOx-2 compared to a conventional Pt on alumina promoter.

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